
Airshed Assessment:
Trace Gases, Particulates
and Agriculture
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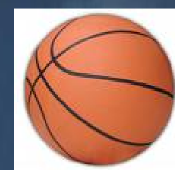
The Air We Breathe

- The world is a basketball, and our atmosphere is a piece of paper covering the ball
- Troposphere
  - Lowest layer in the atmosphere
  - Where we live and breath
- Weight of the molecules in the atmosphere create air pressure
  - Thus, air pressure is reduced at higher elevations



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The Air We Breathe

- Major Components of the Atmosphere
  - 78% Nitrogen (N_2)
  - 20.95% Oxygen (O_2)
  - 0.93% Argon (Ar)
  - 0.04% Carbon Dioxide (CO_2)
  - 1% Water Vapor (H_2O)
  - < 0.08% other trace gases
- It is these trace gases that impact our health and drive atmospheric chemistry

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Trace Gases & Particulate Matter

- Carbon compounds:
  - Volatile Organic Compounds (VOCs)
  - Carbon Dioxide (CO_2)
  - *Carbon Monoxide (CO)*
  - Methane (CH_4)
- Sulfur compounds
  - Hydrogen Sulfide (H_2S)
  - *Sulfur Dioxide (SO_2)*
- Nitrogen compounds
  - Oxides of Nitrogen (NO_x) = NO, NO_2
  - Ammonia (NH_3)
  - Nitrous Oxide (N_2O)
- Particulate Matter
  - Organic
  - Inorganic
- *Halogen-containing compounds (Fluoride, Chloride, Bromine, Iodide)*
- *Radicals*

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Playing by the Rules

- Law of Conservation of Mass
  - Matter cannot be created nor destroyed
  - But, it can change form

- Each element (carbon, nitrogen, oxygen, etc.) does not just disappear or go away
  - Fixing a water problem, usually leads to a soil, air, etc., problem

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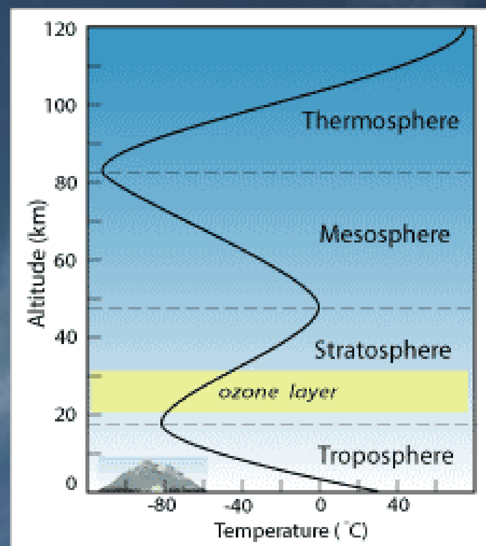
Ozone (O_3)

- Two kinds of ozone
  - Stratospheric ozone layer protects us from harmful UV light
  - Tropospheric ozone that is harmful to human health and vegetation



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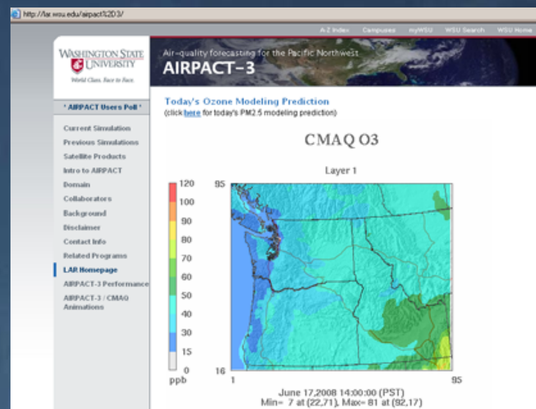
Tropospheric Ozone Chemistry

- Ozone is a "secondary pollutant"
  - Not directly emitted
  - Created in the atmosphere
- VOC + NO_X + sunlight => O_3



- Timescale: 1-2 hours later
  - Ozone typically forms downwind of precursor releases
- http://www.airpact.wsu.edu/

Tropospheric Ozone Chemistry

- NO_2 + sunlight -> NO + O
- O + O_2 -> O_3
- O_3 + NO -> NO_2 + O_2
  - Key: Ozone is generated and consumed

- VOCs + sunlight -> Radicals
- NO + Radicals -> NO_2
  - Key: VOCs provide a pathway to NO_2 regeneration without the destruction of O_3

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Review

- Is Ozone a good thing in the Troposphere?
- Is sunlight necessary for ozone formation? Why?
- What trace gases are necessary for ozone formation?

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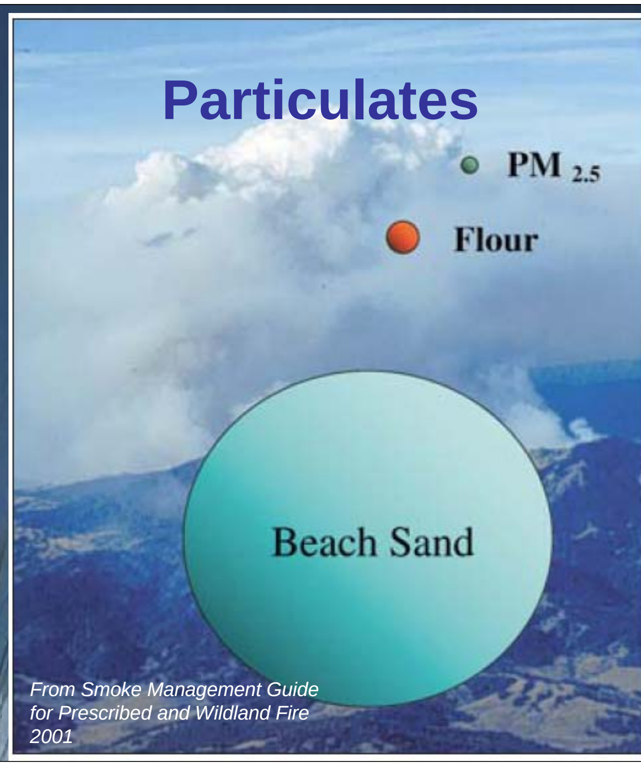
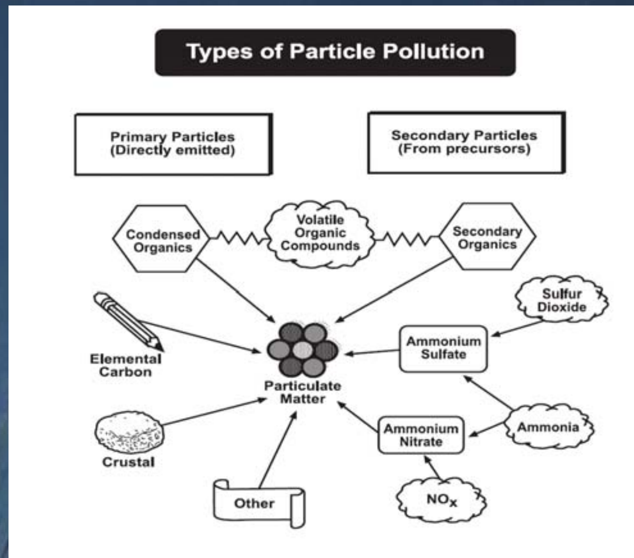
- Fine particulates are also known as aerosols
- Fine particulates play a role in:
  - Atmospheric chemistry
  - Human health impacts
  - Visibility impacts
- Component of smog



From Smoke Management Guide for Prescribed and Wildland Fire 2001

- Particulates are:
  - Emitted directly (primary)
  - Created in the atmosphere (secondary)
- Major particulate species
  - Ammonium Sulfate ($(NH_4)_2SO_4$)
  - Ammonium Nitrate (NH_4NO_3)
  - Organic Carbon (OC)
  - Elemental Carbon (EC)
  - Soil/Dust



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Source: Adapted from Dye, T., C. MacDonald and D. Miller. *Air Quality and Meteorology 101*. Sonoma Technology, Inc. Presentation at U.S. Environmental Protection Agency's 2004 National Air Quality Conference, Baltimore, Maryland. Retrieved June 20, 2005, from http://cfpub.epa.gov/airnow/index.cfm?action=conference2004.aq.

Inorganic Aerosol Chemistry

- Interaction of:
  - Sulfate (SO_4)
  - Nitrate (NO_3)
  - Ammonium (NH_4)
- $NH_3 + SO_2$ + radicals -> $(NH_4)_2SO_4$
  - Preferential reaction
- $NH_3 + HNO_3 \leftrightarrow NH_4NO_3$
  - If excess ammonia

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Nitrogen Chemistry

- NO_2 plays a role in both O_3 and PM formation
- $NO_2 + OH \rightarrow HNO_3$ (nitric acid)
  - Nitric acid deposits quickly
- $NH_3 + HNO_3 \leftrightarrow NH_4NO_3$ (ammonium-nitrate)
  - Temperature dependent reaction
    - Cooler temperatures $\therefore NH_4NO_{3\,(p)}$
    - Warmer temperatures $\therefore HNO_{3\,(g)}$
    - Thus, NH_3 controls effective seasonally (winter)
  - Ammonium-nitrate
    - Less affinity to deposit than HNO_3
    - Can be transported longer distances

Organic Aerosol Chemistry

- VOCs can react with radicals to produce particulate matter
- Terpenes are the major biogenic VOC that can yield particulate matter

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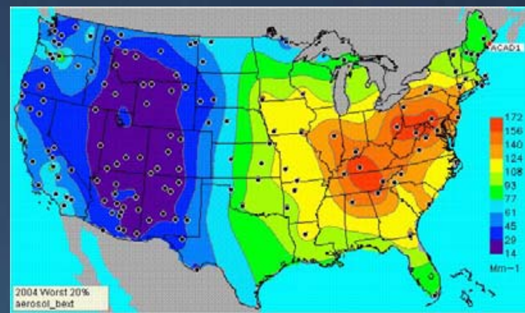
Visibility

- The extinction of light reduces visibility
- $\beta_{ext} = \beta_{scat(g)} + \beta_{scat(p)} + \beta_{abs(g)} + \beta_{abs(p)}$
- IMPROVE monitoring network
- Regional Haze Rule



- Rural vs urban light extinction
  - In rural environments:
    - Typically 90% of β_{ext} is from $\beta_{scat(p)}$ of particulates.
    - EC will $\beta_{abs(p)}$ but it is typically in low concentrations.
  - In urban environments:
    - $\beta_{abs(g)}$ by NO_2 can account for up to 50% of β_{ext}

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Review

- Is PM2.5 smaller or larger than beach sand?
- How does particulate matter get into the atmosphere?
- Can temperature play a role in the formation of particulate matter? How?

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Air Emissions related to NRCS AQAC Resource Concerns

	GHG	PM	O_3 Precursors	Odor
CO_2	√			
CH_4	√			
VOC		√	√	√
NO_x		√	√	
NH_3		√		√
N_2O	√			
H_2S				√
PM		√		

SOx – fuels (low sulfur fuels are being mandated however)

Carbon dioxide (CO_2), Methane (CH_4), Carbon Monoxide (CO)

- Main pathways of formation
  - Microbial/cellular conversion of C compounds
  - Combustion
- Agricultural Sources:
  - Burning (CO, CO_2, CH_4)
  - Animal Operations (CH_4)
  - Engine emissions (CO_2)
  - Tillage of organic soils

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Prefers higher temperatures and moisture content

Note: CO_2 & H_2O are the natural end-products of organic decomposition

N2O has a global warming potential nearly 300 times that of CO2 and constitutes approximately 6% of the anthropogenic greenhouse effect. Approximately 1/3 of global N2O is estimated to occur from soils under natural vegetation and the contribution of agriculture to the total is estimated at approx 35% globally (United Nations Food and Agricultural Organization (FAO) 2001 report).

Nitrification is the biological oxidation of ammonia with oxygen into nitrite (NO2) followed by the oxidation of these nitrites into nitrates (NO3). It is a relatively constant process across ecosystems. Denitrification is the reduction of NO3 or NO2 to gaseous N oxides and molecular N2 by bacteria. It tends to occur in "hot spots." Nitrification/denitrification are the dominant sources of N2O and NO in most systems.

Ammonia (NH_3)

- Main pathways of formation
  - Breakdown of urea by urease enzyme
  - Microbial degradation of N compounds
- Agricultural Sources
  - Animal Operations
    - Manure Management
      - Barns
      - Manure Storage Facilities
  - Land Application of manure
  - Mineral N fertilizers

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Needs basic (pH >7.0) conditions

Prefers higher temperatures and moisture content
Food production contributes more than 50% of the global NH3 emissions

Volatile Organic Compounds (VOCs)

- Main pathways of formation
  - All living organisms emit VOCs naturally
  - Breakdown of biological material
  - Incomplete combustion
  - Volatilization
- Agricultural Sources:
  - Livestock and Livestock Waste
  - Pesticide Application
  - Burning
  - Vegetation (biogenic emissions)
  - Fuels

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VOCs are produced as intermediate compounds in the overall process of decomposition of biological materials, including manure, feed, or animal or plant materials. Any inefficiencies in the decomposition process will yield VOCs rather than the natural end-products (CO2 and H2O).

Volatilization from organic-based liquids

Oxides of Nitrogen (NO_X)

- Pathways to formation
  - Combustion
  - Nitrification/Denitrification
- Agricultural Sources
  - Engines (Farm equipment, pumps, diesel trucks, off-road equipment, etc.)
  - Livestock and Livestock Waste
  - Pesticide Application
  - Burning
  - Natural Soil Emissions
  - Breakdown of biological materials (manure, feed)
  - Ammonia-based fertilizer

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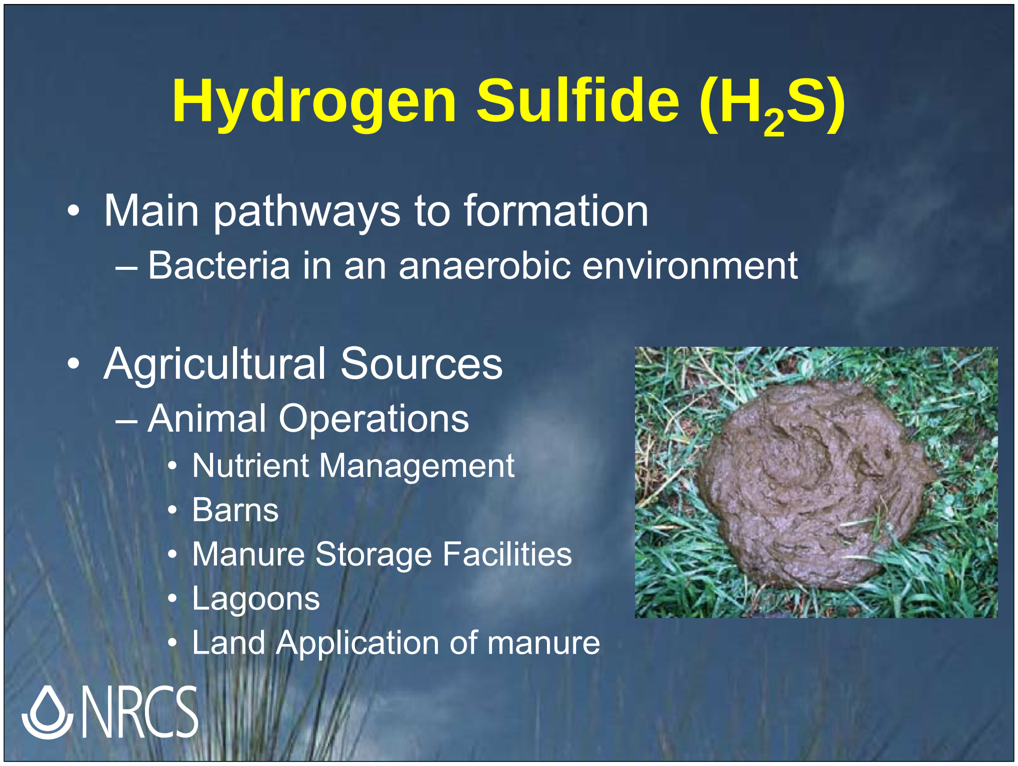
NOx is typically a product of the combustion process, with nitrogen from either the fuel or air combining with oxygen from the air.

NOx can also be formed by microbial activity, mainly the nitrification and denitrification processes, including the decomposition of biological material or the transformation of inorganic nitrogenous compounds.

- The nitrification/denitrification of nitrogen-containing biological material, such as manure, feed, or animal or plant materials, can lead to natural emissions of NOx.

- The nitrification/denitrification of inorganic nitrogen sources, such as ammonia-based fertilizer, can also lead to emissions of NOx.

According to the United Nations Food and Agricultural Organization (FAO) 2001 report, fossil fuel combustion and industrial processes account for approximately 40% of global NOx emissions, soils under natural vegetation account for approximately 22% of NOx emissions, lightning 21% and biomass burning 15%.



Desulfovibrio desulfuricans, **found in the digestive tract of both man and animals, is the most common bacteria which produce H_2S under anaerobic conditions. These obligate anaerobes use sulfate as their oxygen source, ammonia as their sole source of nitrogen, and various forms of organic matter as a food supply including amino acids, carbohydrates, organic acids, etc., when in an oxygen limited environment. These reactions often take place in the slime layer on collection pipes and in the sludge of lagoons, etc.**

Sulfate ion + organic matter > ***d.d. bacteria*** > elemental sulfur + water + carbon dioxide**SO_4^{2-} + CH_4 > *d.d. bacteria* > S + $2H_2O$ + CO_2**

http://www.rancocas-usa.com/Prev_of_Hydro_Sulfide.html

Particulate Matter (PM)

- Main pathways of formation
  - Direct emission: combustion, soils
  - Secondary Formation: rxn of NO_X, NH_3, VOCs, SO_2
- Agricultural sources
  - Dust
    - Feedlots
    - unpaved roads
    - tillage operations
    - exposed soil surfaces (wind erosion)
  - Fire
  - See agricultural sources of NO_X, NH_3 and VOCs

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